

11/4/49 U.S.

Samples have been furnished in this case under Section 2, Sub-section 5.

PATENT SPECIFICATION =DE 540 409

(2)



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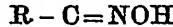
COMPLETE SPECIFICATION.

Processes for Preparing Tetrazoles.

I, ALBERT BOEHRINGER, a German Citizen, sole owner of the Firm C. H. Boehringer Sohn, of Nieder-Ingelheim a/Rhein, Germany, do hereby declare the 5 nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention is an improvement in or modification of the process according to the prior Application No. 10 280,529, wherein tetrazoles are prepared from esters of oximes, especially from their sulphonic acid esters or from the 15 so-called Beckmann transformation products of the said compounds, by the action of azides or of free hydrazoic acid in the absence of concentrated mineral acids.

20 It has now been furthered found that amino-substituted tetrazoles can be obtained by bringing esters of amido-oximes, particularly their sulphonic acid esters, or Beckmann transformation products of the said substances, into reaction 25 with azides or free hydrazoic acid, or by treating the said amido-oximes themselves in the presence of hydrazoic acid with substances, such as thionyl chloride, 30 phosphorus pentachloride, phosphorus oxychloride and the like, which form esters with the amido-oximes, the said esters then undergoing the Beckmann transformation. In this way, from 35 amido oximes of the formula



C-aminotetrazoles are obtained.

In carrying out the process sodium azide or free hydrazoic acid is employed 40 in at least a molecular proportion or in excess thereof. When possible the reaction is effected in an aqueous alkaline solution, otherwise an organic solvent, with or without the addition of basic 45 reacting substances, is employed in the absence of concentrated mineral acids.

Tetrazoles have been prepared by treating carbonyl compounds with an excess

[Price 1/-]

of hydrazoic acid in the presence of acid catalysts such as phosphorus pentoxide, 50 zinc chloride, ferric chloride, phosphorus pentachloride, phosphorus oxychloride, aluminium chloride, thionyl chloride. C-Amino-tetrazole has been prepared by Thiele from amino-guanidine (Liebig's Annalen der Chemie vol. 270—1882— 55 Page 12 and German Patent 65584). Wieland (Berichte der Deutschen Chemischen Gesellschaft Vol. 42 page 4201) obtained N-oxytetrazole by acting on hydrazidoxime with nitrous acid. Forster (Chemisches Centralblatt—1909—vol. 1, page 1316) also produced N-oxytetrazole by acting on hydroximic acid chloride with sodium azide. Freund (Berichte der Deutschen Chemischen Gesellschaft, vol. 34, page 3110) prepared C-oxytetrazole by a complicated process from thio-semicarbazide. 60 65

The following examples serve to illustrate the invention:—

1. 1 mol. of phenylacetic-amido-oxime is esterified in aqueous alkaline solution whilst cooling with 1 mol of benzene sulphonate acid, the ester obtained is boiled under reflux with 50% alcohol and 1.2 mol of sodium azide. The reaction mixture is recrystallised from 95% alcohol, when thin colourless needles having a melting point of 191° C. are obtained, 70 which are identical with the N-benzyl-C-aminotetrazole (5-amino-1-benzyl- 1, 2, 3, 4-tetrazole) obtained by Thiele by benzylating C-amino-tetrazole. Yield 70% of theory. 75 80 85

2. 1 mol of benzyl-amidoxime is dissolved in 100 c.c. of water, 1.5 mol of sodium hydroxide being added, esterified whilst cooling with 1 mol of benzene sulphonate chloride, after $\frac{1}{2}$ to 1 hour treated with 150 c.c. of alcohol and 1.2 mol of sodium azide and boiled under reflux for a fairly long time. The reaction product crystallises from alcohol in the form of compact crystals of melting point 159° C. The figures obtained on analysis accord 90 95 with the formula $C_6H_7N_5$ of 1-phenyl-5-amino-1, 2, 3, 4-tetrazole. The chemical

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behaviour corresponds with the known C-amino-tetrazoles. Yield 80% of theory.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. An improvement in or modification of the process for preparing tetrazoles according to Specification No. 280,529, wherein esters of amido-oximes or transformation products of the said substances are treated with azides or with free hydrazoic acid in the absence of concentrated mineral acid.

2. A process according to claim 1, wherein amido-oximes are treated in the presence of hydrazoic acid with substances

such as phosphorus oxychloride, which form esters with the amido-oximes, the 20 said esters then undergoing the Beckmann transformation.

3. A process according to claim 1, wherein the esters are sulphonic acid esters.

4. The process for preparing amino-tetrazoles substantially as described with reference to the accompanying examples.

5. Amino-tetrazoles when prepared by the processes claimed in any of the preceding claims.

Dated this 3rd day of February, 1928.

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